

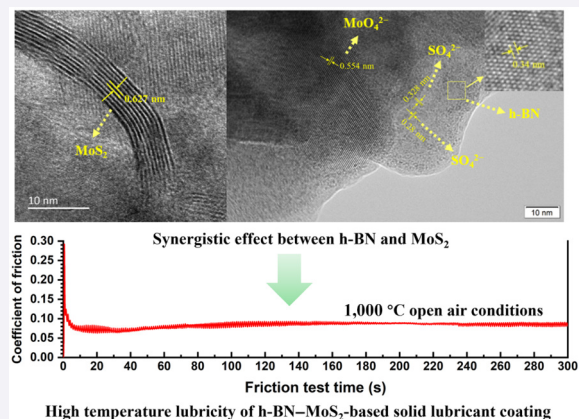
Synergistic effect between h-BN and MoS₂ for excellent lubrication of solid lubricant coating for high-temperature, open-air-system applications

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ABSTRACT: High-temperature solid lubricant coatings with decent lubrication performance are essential in critical processes of metal forming and aerospace. However, their preparation is formidably challenging due to the harsh working conditions. Here, we successfully developed a solid lubricant coating via a facile and eco-friendly approach by casting a homogeneous mixture of molybdenum disulfide (MoS₂) and hexagonal boron nitride (h-BN) as lubricants, silicate as the binder, and water as the solvent onto a titanium alloy substrate. This solid lubricant coating exhibited excellent and stable tribological properties with a very low coefficient of friction (COF) of 0.080 at 1,000 °C, yet in an open-air atmosphere. This superior lubrication behavior is attributed to the synergistic effect between the base lubricants h-BN and MoS₂, contributing to the formation of a coating for both lubrication and lubricant protection against oxidation at 1,000 °C in an open-air environment. This work largely extends the operation temperature range of the crucial lubricant MoS₂ in an open-air atmosphere and further sheds valuable light on the design of high-temperature solid lubricants via the synergistic effect between base lubricants.

KEYWORDS: h-BN–MoS₂-based solid lubricant coating; high temperature; open-air atmosphere; excellent lubricating performance; synergistic effect



1 Introduction

Solid lubricant coatings are commonly employed in systems operating under large temperature extremes or variations, such as cryogenic sensors, turbopumps for LH₂/LOX fuel engines, and metal forming processes [1]. With the rapid development of the aerospace industry, solid lubricant coatings used for much harsher working conditions, including a relatively wide range of operating temperatures, ambient pressures, and multiple service environments, are required [2, 3]. In pursuit of expanding the operation conditions in terms of temperature and pressure, the strategy for designing solid lubricant coatings has evolved from the initial single-phase-based coatings exemplified by graphite [4], transition-metal dichalcogenides (TMDs) [5], polytetrafluoroethylene (PTFE) [6], hexagonal boron nitride (h-BN) [7], etc. to multiphase-based coatings [8–30], such as SiO₂–graphite–Al(PO₃)₃ [31], Ag–BaF₂/CaF₂–Cr₃C₂–NiCr [32], ZrO₂–h-BN–SiC [33], Ni₃Al–Ag–V₂O₅ [34], and even nanocomposite chameleon coatings [35].

Despite the complexity of solid lubricant coatings, their base lubricants play a vital role in high-temperature lubrication. To date, graphite, molybdenum disulfide (MoS₂), h-BN, and PTFE still dominate the market of base lubricants, among which MoS₂ and h-BN have the potential for high-temperature applications. MoS₂ crystallizes in a quasi-two-dimensional (2D) layered structure [36], where the strong in-plane covalent bonding combined with the weak out-of-plane van der Waals interactions of S–Mo–S planes (with a low shear strength of 1–2 MPa) enables smooth shearing and low friction at the transfer film between the coating and counterpart under different application environments [37]. Upon friction, the sliding direction follows the friction-induced orientation of the (0001) basal planes of MoS₂ grains [37], the corresponding higher surface energy leads to a higher resistance to oxidation and water absorption than edge facets do, and consequently enables relatively high stability under the shearing force [38]. Nevertheless, exposure to the shearing force under high-temperature (> 400 °C) operation conditions results in a substantial loss of shearing planes (0001) due to temperature-

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induced oxidation, leading to an increase in adhesive forces in the friction contact, a reduction in cohesive strength within the bulk film, the introduction of blisters, and the generation of relatively large wear debris [35]. Subsequently, the debris is pushed out of the transfer film and gives rise to direct contact between the counterpart and substrate, significantly deteriorating the lubrication effect, which largely restricts the high-temperature application of MoS₂ lubricant. Given this, intensive research in the last few decades has been conducted to enhance the tribological behavior of MoS₂ over a wide temperature range, especially at high temperatures.

Based on the lubrication degradation mechanism, the basic goal of increasing the lubrication and lifespan of MoS₂-based coatings at high temperatures is to modify their surface to reduce water- and oxygen-induced oxidation via the introduction of additives to prepare composite coatings by leveraging the synergistic effect among coating components. Nainaparampil et al. [39] reported an increase in the wear life of laser-ablated MoS₂ films with simultaneous magnetron sputtering of Al additives under humid conditions, which is attributed to the synergistic effect whereby the formation of alumina creates an adhesive and lubricating mixture of wear debris under tribostress in humid surroundings. Hu et al. [40] reported a much longer wear life of multilayered MoS₂-Sb₂O₃ composite films than that of pure MoS₂ films in air with 40% relative humidity, which was attributed to the preservation of discharged fresh MoS₂ and the inhibition of crack propagation perpendicular to the interface. Gardos [41] reported that the introduction of a graphite additive can extend the wear life of burnished or bonded MoS₂ layers and revealed that the smoother basal planes of oxidized graphite prolong interlaminar shear and postpone film interlocking, which promotes intercrystalline slip and diffusion barrier formation and consequently increases the wear life in a synergistic mode. Kong et al. [42] reported a ZrO₂-MoS₂-CaF₂ self-lubricating composite with good lubrication performance at 1,000 °C yet under a low force of 10 N in ambient air by utilizing a synergistic effect between MoS₂ and CaF₂. Shi et al. [43] prepared NiAl matrix self-lubricating composites with MoS₂ and Ti₃SiC₂ lubricants, which displayed excellent self-lubricating performance over a wide temperature range from room temperature to 800 °C under a loading of 10 N in a pure Ar protection atmosphere due to the synergistic effect between MoS₂ and Ti₃SiC₂. In general, operating conditions, including a high vacuum, inert gas atmosphere (dry Ar atmosphere), and mild temperature range (< 400 °C), are required for a low-friction MoS₂-based composite coating. To the best of our knowledge, its superior lubricity in an open-air and high-temperature environment has rarely been reported.

h-BN has a lamellar crystalline structure, where molecules within each layer are bonded via covalent bonds, whereas adjacent layers are bonded through weak van der Waals forces [44]. Owing to these structural properties, h-BN can be easily sheared along its basal plane and is commonly used as a good solid lubricant [45]. Chen et al. [17] prepared h-BN/SiC solid lubricating composite materials via spark plasma sintering technology, which exhibited decent lubricating performance over a wide temperature range from room temperature to 900 °C. At 900 °C, the COF ranged from 0.26 to 0.34, and the higher the h-BN content was, the lower the COF was. The same technique was used to prepare the ZrO₂/h-BN/SiC solid lubricating composite materials, in which h-BN was the main reason for the reduction in the COF. At 900 °C, the COF of the material was approximately 0.47 [33]. However, the reported friction tests were carried out under high vacuum, largely limiting their application.

In pursuit of a solid lubricant coating for high-temperature,

ambient-atmosphere applications, we chose MoS₂ and h-BN as base lubricants and prepared a solid lubricant coating via a facile, aqueous solution-based, and eco-friendly method by casting a uniform mixture of base lubricants, metasilicate binder, and water solvent onto the titanium alloy substrate at room temperature. The prepared coating exhibited superior lubrication behavior with a very low COF at 1,000 °C in an open-air system. A series of complementary techniques, including thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and transmission electron microscopy (TEM), were used to investigate the fundamental mechanism underlying the excellent lubrication behavior, which revealed that the synergistic effect between MoS₂ and h-BN that promotes the formation of a condensed coating for lubrication and lubricant protection against oxidation leads to excellent lubrication behavior. This work demonstrated a feasible way to expand the operation temperature range of MoS₂ as a key lubricant in an open-air system.

2 Results and discussion

2.1 Tribological results

The tribological performance of the MoS₂-based coating, h-BN-based coating, and h-BN–MoS₂-based composite coatings with different weight fractions of h-BN and MoS₂, as well as the reference binder coating, was evaluated via friction tests in an open-air system at 1,000 °C, which was described by the profiles of the COFs (Figs. S1 and S2 in the Electronic Supplementary Material (ESM)) and the average COF values (Tables S1 and S2 in the ESM). Figure S1 and Table S1 in the ESM show that the composite coating with 2 wt% h-BN and 4 wt% MoS₂ displayed the best lubrication behavior, indicating that the optimal weight fractions of h-BN and MoS₂ in the h-BN–MoS₂-based composite coating were 2 and 4 wt%, respectively. Therefore, the 2 wt% h-BN–4 wt% MoS₂-based composite coating was the focus of this study. To simplify the notation, the 2 wt% h-BN–4 wt% MoS₂-based composite was denoted as the h-BN–MoS₂-based composite coating in the following discussion. Friction tests of different coatings were repeated to verify the experimental reproducibility, and the consistency of the plots of the same coating strongly confirmed that our results were accurate and reliable, as shown in Fig. S2 in the ESM. The tribological performance of the h-BN–MoS₂-based composite coating was compared with that of the control samples (the binder coating, h-BN-based coating, and MoS₂-based coating), as shown in Fig. 1 and Table S2 in the ESM. In general, the COF profiles can be generally divided into three regions: the run-in period, the steady period, and the failure period. All the samples demonstrated a very short run-in period with a gradual decrease in the COF values within a few seconds. During the run-in period, the COF of the binder coating initially reached approximately 0.1, followed by a slight decrease to 0.08 after 20 s of the test before entering a very narrow steady period of ~5 s, and then a gradual increase with severe fluctuation until the end of the test, termed the lubrication failure phenomenon. The tribological behavior of the MoS₂-based coating was analogous to that of the reference binder: It displayed an initial COF of ~0.2 in the run-in period, which increased dramatically to 0.26 in a few seconds, then gradually decreased to 0.10 after 20 s and remained constant in the steady period until 60 s, and eventually fluctuated until the end of the test, with an average COF of 0.188. For the h-BN-based coating, the COF

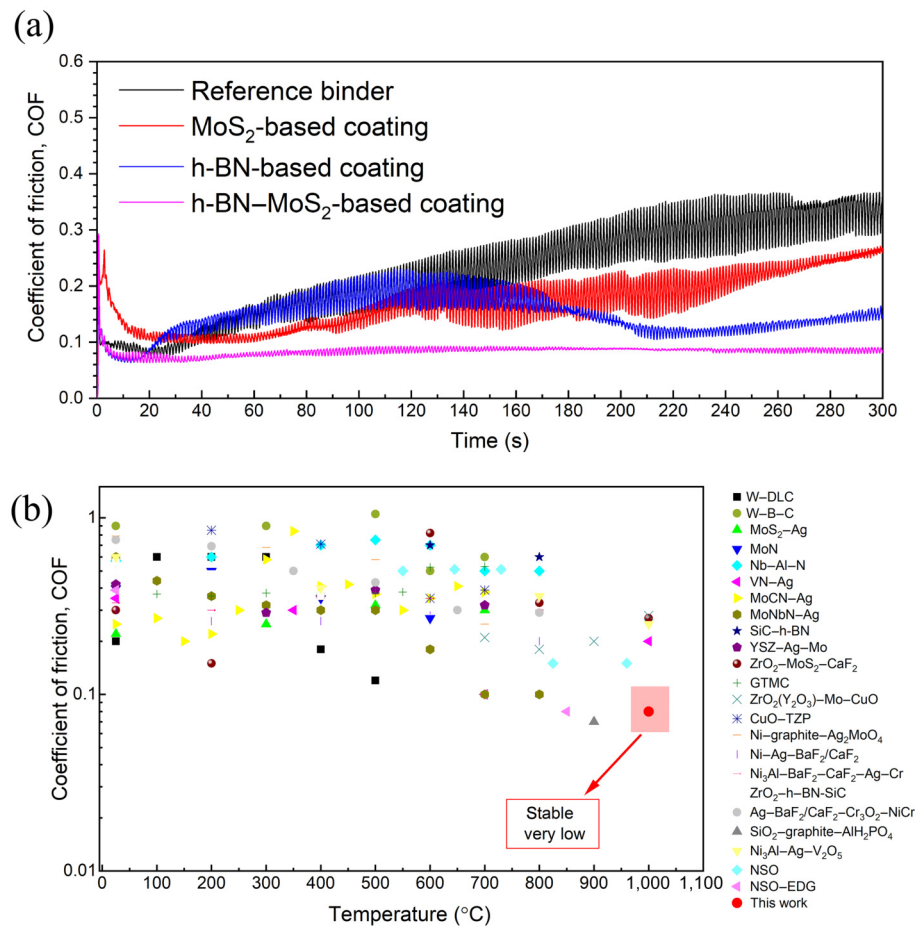


Fig. 1 (a) Profile of COFs of prepared coatings and reference binder as a function of friction test time in an open-air system at 1,000 °C. (b) Comparisons of COFs of this work with those reported in Refs. [8–15, 17, 19, 22–29, 31–34, 42] at temperatures ranging from 25 to 1,000 °C: h-BN-MoS₂ composite coating (see highlighted value) displays the lowest COF at 1,000 °C even in an open-air environment.

decreased drastically to 0.07 in just a few seconds during the run-in period, remained constant for a few seconds during the steady period, then experienced an undulatory increase to 0.22 at 120 s, a fluctuating decrease to 0.12 at 220 s, a slight increase to 0.14 at the end of the friction test, and an average COF of 0.131. In comparison, the h-BN-MoS₂-based composite coating behaved distinctly from the reference binder-, h-BN-, and MoS₂-based coatings. Its COF decreased from 0.13 to 0.07 in just a few seconds at the beginning and then remained almost constant until the end of the friction test without the emergence of the tribology failure period, with an average COF value of 0.08, reflecting excellent tribological behavior. To demonstrate the outstanding tribological performance of the h-BN-MoS₂-based coating, its COF was compared with the literature data from friction tests performed in rotational mode at temperatures ranging from 25 to 1,000 °C (Fig. 1(b)), and detailed test conditions can be found in Table S3 in the ESM. The high-temperature lubrication performance of the h-BN-MoS₂ composite coating studied here at 1,000 °C in an open-air atmosphere was likely superior to that reported thus far [8–15, 17, 19, 22–29, 31–34, 42]. While the wear resistance of a coating can generally reflect the tribological behavior of the coating, the measurement of the wear resistance in this work is challenging (see Supplementary Note S1 and Figs. S3–S5 in the ESM), and consequently, the wear resistance performance is not reported herein.

In addition, the image of the disc after the friction test, to some extent, can also be an indicator of the tribological behavior of the coating (Fig. S6 in the ESM). Severe delamination clearly occurred

in the whole region of the MoS₂-based coating, suggesting poor adhesion between the substrate and coating, which was attributable to the increased COF. However, for the rest of the coatings, intact coatings remained without delamination and dense tribo-film layers formed during the friction test. Nevertheless, only the h-BN-MoS₂-based coating displayed a more consistent morphology inside and outside of the worn regions, which was attributed to its outstanding lubrication performance and was in good agreement with the observed low COF during the whole friction test. Overall, the comparison clearly demonstrated the excellent tribological performance of the h-BN-MoS₂-based composite coating at 1,000 °C even in an air atmosphere.

2.2 Thermal behavior analysis

To understand the underlying fundamentals of the low COF displayed by the h-BN-MoS₂-based composite coating, a comparative study was performed via a series of characterization techniques. We first employed *in situ* TG-FTIR technology to study the thermal behavior of the coatings by mimicking the same atmospheric conditions as those used in the friction tests (Figs. 2 and 3). Notably, the observed absorption peaks of CO₂ in the FTIR spectra were due to an incomplete background subtraction effect, which did not affect our analysis. For the single-phase h-BN-based coating, the total weight experienced a steep loss of up to 28% of the original mass before 400 °C (Fig. 2(a)), which was mainly due to volatilization of the adsorbed water and crystallization water from the coating, as indicated by FTIR results

(Fig. 3(a1)). There was little weight loss during the period when the temperature increased from 400 to 1,000 °C and during the subsequent 30 min of holding at 1,000 °C, which is consistent with the lack of observable FTIR peaks associated with the oxidation of h-BN. (Figs. 3(a2) and 3(a3)), indicating little oxidation of h-BN. The thermal gravity behavior of the reagent h-BN was then tested under the same experimental conditions as those used for the friction test to study the protection effect of the prepared coating (Fig. 2(b)). The weight of the reagent h-BN remained constant until 920 °C, gradually increased from ~920 to 1,000 °C, and then rapidly increased during the holding period, with a total mass of 119.4% of the pristine state. The absorption peaks of N_2O were detected during the temperature holding period, indicating that

the oxidation of h-BN was responsible for the mass increase in h-BN above ~920 °C (Fig. 2(b) and Fig. S7(a) in the ESM). A comparison of the TG-FTIR behavior between the h-BN-based coating and the reagent h-BN indicated that the coating could protect h-BN from oxidation under air.

Analogous to the TG behavior of the h-BN-based coating, the weight loss of the MoS_2 -based coating mainly occurred before 400 °C, with a loss of ~21.7% (Fig. 2(a)) due to the emanation of water vapor from the coating, reflected by the corresponding FTIR spectra (Fig. 3(b1)). When the temperature increased from 450 to 1,000 °C, the TG profile tended to fluctuate, with a mass increase of approximately 3%, which was attributed to the oxidation of MoS_2 as indicated by the emergence of absorption

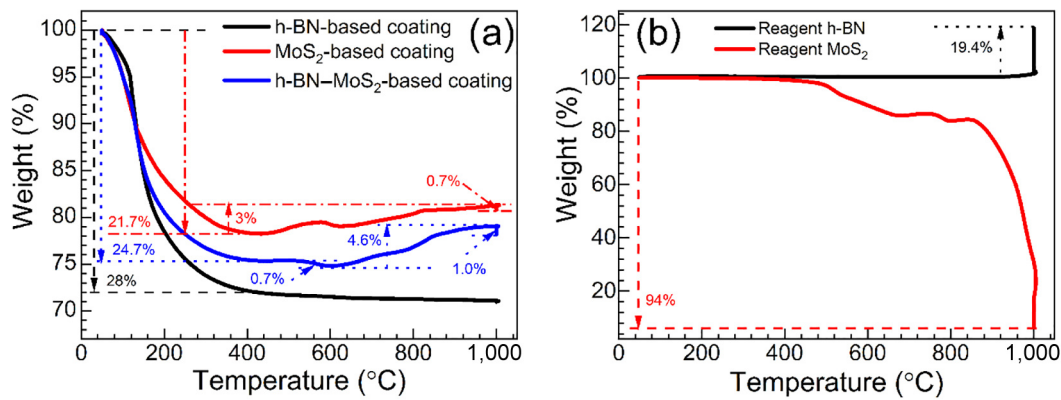


Fig. 2 Thermal gravity analysis results of (a) different coatings and (b) reagents h-BN and MoS_2 .

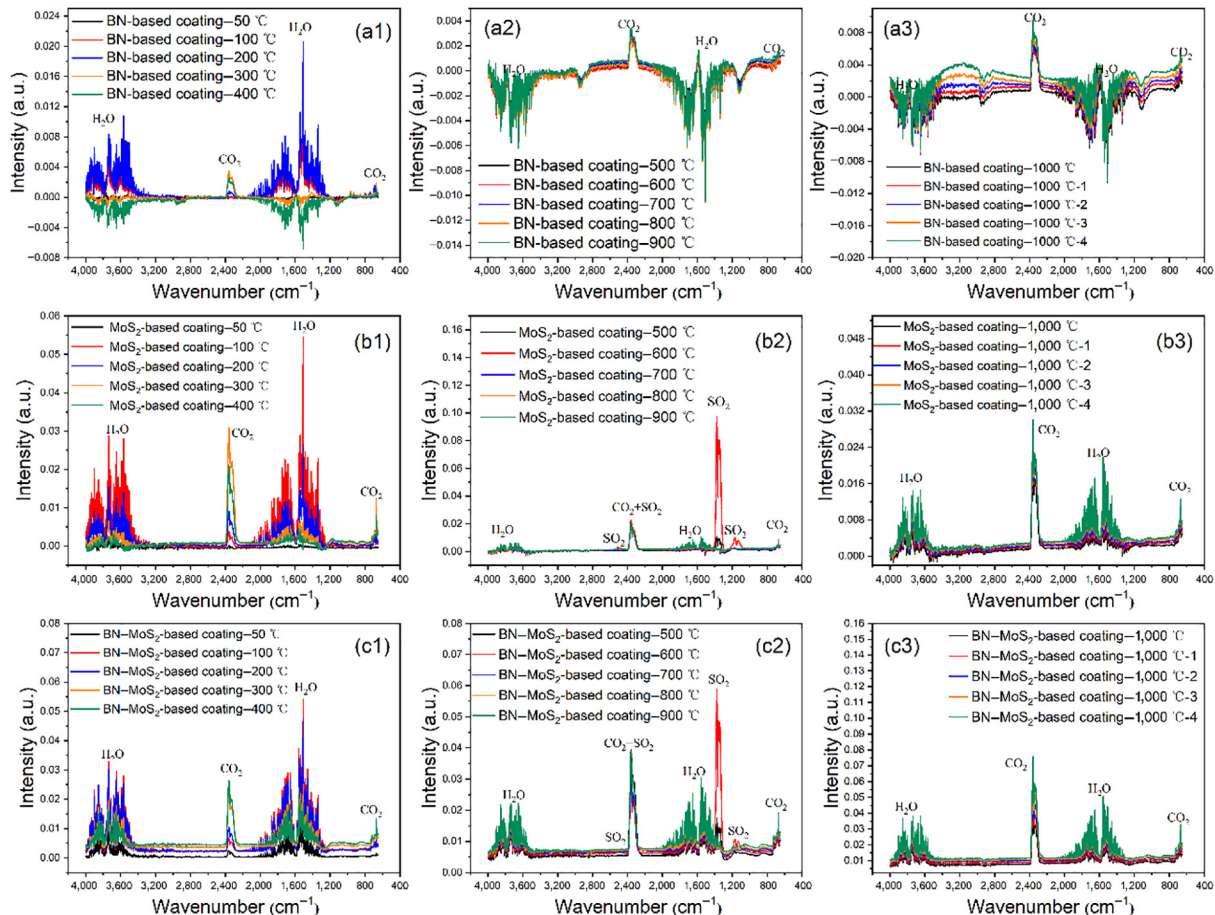


Fig. 3 In situ FTIR spectra of (a1–a3) h-BN-based coating, (b1–b3) MoS_2 -based coating, and (c1–c3) h-BN- MoS_2 -based composite coating as a function of temperature.

peaks of SO₂ in FTIR spectra (Fig. 3(b2)). When held at 1,000 °C, the MoS₂-based coating experienced a slight weight loss of ~0.7%, possibly because of volatilization of the oxidation products (Fig. 3(b3)). In comparison, the TG–FTIR evolution of the reagent MoS₂ was distinct (Fig. 2(b) and Fig. S7(b) in the ESM). The mass of MoS₂ remained nearly invariant before 400 °C, as deduced by small changes in the FTIR absorption peaks of water vapor, and then gradually decreased with temperature until 670 °C, which was mainly due to the intensive oxidation of MoS₂, as evidenced by a prominent increase in the SO₂ FTIR absorption peaks at 600 °C, which then remained relatively constant until 850 °C, as indicated by tiny changes in the FTIR absorption peaks of H₂O and SO₂. Finally, the peak mass decreased significantly above 850 °C, with an overall loss of ~94%, which was probably due to the volatility of the oxidation products of MoS₂ at high temperatures. The comparison of TG–FTIR behavior between the MoS₂-based coating and the MoS₂ reagent indicated that the coating can protect MoS₂ against continuous oxidation under air and high-temperature conditions.

In terms of the h-BN–MoS₂-based composite coating, the TG profile and FTIR spectra varied in a similar fashion to those of the MoS₂-based coating (Figs. 2(a) and 3(c)). The mass decreased dramatically before 400 °C, with a mass loss of ~24.7% due to the volatilization of the adsorbed and crystallized water, as indicated by the increased intensity of FTIR absorption peaks of H₂O. The mass loss remained almost constant at 500 °C, a slight loss of ~0.7% occurred between 500 and 600 °C due to SO₂ emitted from the oxidation of MoS₂ based on the emergence of SO₂-related absorption peaks in FTIR spectra, increased by ~4.6% during the ramp period from 600 to 1,000 °C, and finally decreased by ~1.0% during the temperature holding period due to the oxidation of MoS₂ and volatilization of the corresponding products. A comparison of the thermal gravity behavior between MoS₂-based and h-BN–MoS₂-based composite coatings revealed that the

difference lies in the different amounts of water vapor lost before 400 °C, which possibly affects the tribological behavior due to the extent of the reaction between MoS₂ and H₂O [36].

2.3 Morphological and elemental distribution analysis

The surface morphology and corresponding elemental distribution of the prepared coatings after the friction test in an open-air system at 1,000 °C were then studied via SEM and EDS (Fig. 4 and Figs. S8–S10 in the ESM). First, the contact area in the Si₃N₄ ball after the friction test was evaluated, and the corresponding analysis demonstrated that Si and N in the Si₃N₄ ball had little effect on the analysis of the coating (Fig. S11 in the ESM). The SEM images revealed that the surfaces of the wear scars can be generally divided into two regions: Region (I) was smooth, and region (II) was relatively rough. For the reference binder-based coating, strip-like regions (II) were predominant in the wear scar, whereas scattered regions (I) featuring microscale porosity were observed (Fig. S8(a) in the ESM). The EDS results demonstrated the highest concentration of Si in region (I) (Fig. S8(d) in the ESM), reflecting a predominance of metasilicate, and a high concentration of Ti in region (II) (Fig. S8(e) in the ESM), indicating a presence of titanium oxide TiO₂ after the friction test. This elemental analysis indicated that the reference binder-based coating has little shielding effect on the substrate during the friction test, which is consistent with the large COF. For the MoS₂-based coating, region (II) again dominated the wear scar with the main elements of Mo and/or S, and region (I) was rich in Si and Ti, indicating its main components of silicate and TiO₂ (Fig. S9 in the ESM). For the h-BN-based coating, the strip-like TiO₂ spread through the entire wear scar (Figs. S10(a)–S10(c) in the ESM). Compared with region (II) (Fig. S10(e) in the ESM), there was more Si in region (I) (Fig. S10(d) in the ESM), indicating that silicate covered part of the TiO₂ in region (I). For the h-BN–MoS₂-based coating, region (II), which predominated

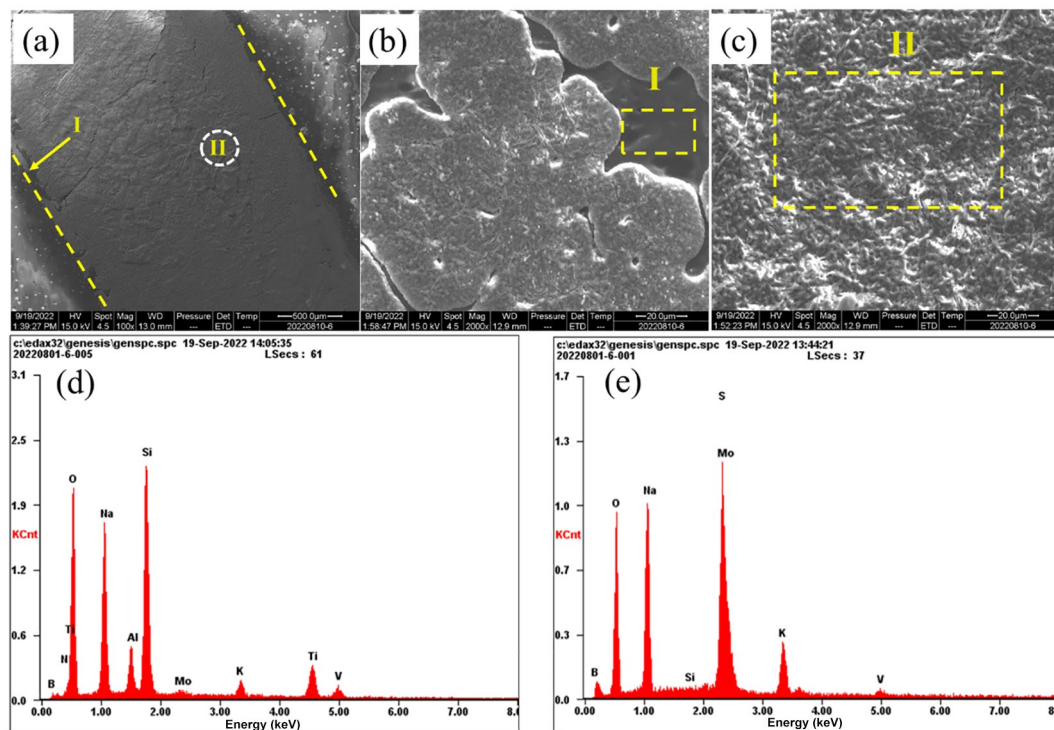


Fig. 4 (a–c) SEM images and (d–e) EDS spectra of wear regions of the h-BN–MoS₂-based coating collected after the open-air friction test at 1,000 °C. (b, c) are zoomed in from (a) to highlight region (I) and region (II), respectively. The EDS spectrum in (d) shows the elemental information of region (I), and the EDS spectrum in (e) shows the elemental information of region (II).

the wear scar surface, displayed an absence of the strip-like TiO_2 (Fig. 4(a)) and was rich in Mo and/or S (Fig. 4(e)), whereas region (I) constituted only a minor part of the wear scar surface (Fig. 4(b)) and was abundant in Si (Fig. 4(d)), indicating its main component of metasilicate.

Given the peak overlap between Mo and S in EDS spectra and the potential loss of S during the friction test, the presence of the detected S in both the MoS_2 - and h-BN- MoS_2 -based coatings is further verified in the following sections. Notably, the lighter atomic mass of element B makes its detection unreliable via EDS. Moreover, the energy overlap between N and Ti also makes probing element B on the surface difficult. In addition, the absence of the observable element N on the wear surface of both the h-BN- and h-BN- MoS_2 -based coatings might be ascribed to the tiny amount of remaining N due to the loss of N in the form of nitrogen oxides from oxidation during the friction test. Therefore, other characterization techniques needed to probe element B in both h-BN- and h-BN- MoS_2 -based coatings will be discussed in the Raman, XPS, TOF-SIMS, and TEM sections.

Considering the difficulty in detecting elements B and N on the wear surface of both h-BN- and h-BN- MoS_2 -based coatings, SEM and corresponding EDS mapping were employed to study the non-wear regions after the friction test at 1,000 °C (Fig. 5 and Fig. S12 in the ESM). Relatively large particles of h-BN were observed in the non-wear region of both the h-BN- and h-BN- MoS_2 -based coatings. EDS mapping revealed a uniform distribution of all the elements except for B and N, both of which were enriched in large particles. During the heating process, h-BN particles aggregated as the particle size increased from the initial nanoscale to the microscale. The larger particles were then confirmed via TEM analysis to be layered hexagonal BNs with interplanar distances of 0.346 and 0.343 nm corresponding to the (002) lattice spacing (Fig. S13 in the ESM) [46]. A comparison study with the morphology of the initial coating verified that this particle aggregation was associated with the friction test. In conclusion, the existence of the layered h-BN reflected that the h-BN in the non-wear regions of the coating was not influenced by the high-temperature friction test.

In addition to the existence of Mo, S, B, and N from the shallow surface characterization study, the cross section of the sample after the friction test was probed to study its morphology and elemental distribution in the wear and non-wear regions (Fig. 6 and Fig. S14 in the ESM). First, the samples were prepared via the electric spark linear cutting technique, followed by a sequence of cleaning, drying, mounting, and polishing procedures. The well-prepared sample was mounted onto the SEM sample stage for testing.

For the MoS_2 -, h-BN-, and h-BN- MoS_2 -based coatings, the element Na preferred to accumulate on the surface of worn regions, and the other elements tended to distribute uniformly

across the whole cross-sectional region (Fig. 6 and Fig. S14 in the ESM). Specifically, the elements Mo and S in the cross section of the MoS_2 -based coating displayed an even distribution and noticeable accumulation in the joint region between the coating and substrate (Fig. S14(a) in the ESM). The surface morphology of the worn region before and after the linear cutting procedure was compared (Figs. S15(a) and S15(b) in the ESM), revealing an absence of delamination and strong adhesion between the lubricant coating and substrate, indicating that the EDS mapping of the cross section could reliably reflect the elemental distribution inside the coating. For the h-BN-based coating, element B was nonuniformly detected across the cross-sectional region, yet with pronounced aggregation at the boundary between the coating and substrate, and the N observed herein could not reflect the true information in the h-BN lubricant because the peak overlap between N and Ti in the EDS mapping and the N adsorbed from the air (Fig. S14(b) in the ESM). Given this, the existence of N in the coating is further discussed in XPS, TOF-SIMS, and TEM sections. In terms of the h-BN- MoS_2 -based coating, the EDS mapping of Mo and S demonstrated a roughly uniform distribution across the cross-sectional region, yet there was a noticeable accumulation in the boundary region between the coating and substrate (Fig. 6). Owing to the intrinsic character of B and N, their true information could not be reliably reflected by EDS mapping, analogous to that of the h-BN-based coating, and they will be further discussed in XPS, TOF-SIMS, and TEM sections. The morphology of the wear scar of the coating after the electric spark linear cutting technique was also analyzed via SEM (Figs. S15(c) and S15(d) in the ESM). The morphology of the worn region drastically varied after the linear cutting treatment, with almost complete delamination of the Mo-rich region, consequently leading to undetected aggregation of Mo on the surface via EDS mapping from the cross-sectional side.

Compared with the nonuniform elemental distribution of wear regions in the MoS_2 -, h-BN-, and h-BN- MoS_2 -based coatings, however, all the other elements except for B and N were distributed evenly in the non-wear track areas of the coatings (Fig. 7 and Fig. S16 in the ESM), indicating that the prepared coatings remained intact in the absence of friction shear force even at high temperatures. Elements B and N were detected in both the h-BN-based and h-BN- MoS_2 -based coatings (Fig. 7 and Fig. S16(b) in the ESM), indicating the existence of h-BN. Despite such similarities, a discrepancy between those two coatings can be observed. For the h-BN-based coating, the morphology and particle size of the detected h-BN in the cross section were consistent with those of the reagent h-BN. However, distinguishing the h-BN only based on the morphology and particle size from the SEM image of the h-BN- MoS_2 -based coating was difficult (Fig. 7(a)), indicating that h-BN had fused

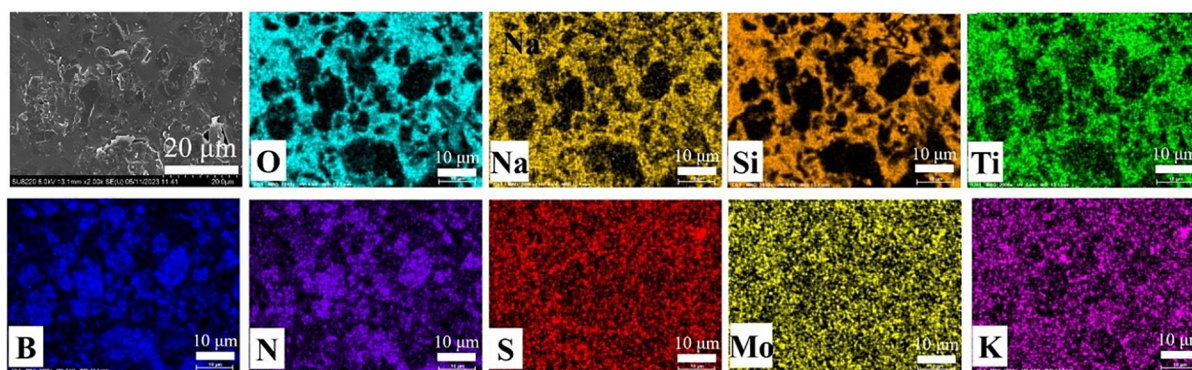


Fig. 5 SEM images and EDS mapping of non-wear regions of h-BN- MoS_2 -based coating after the friction test at 1,000 °C.

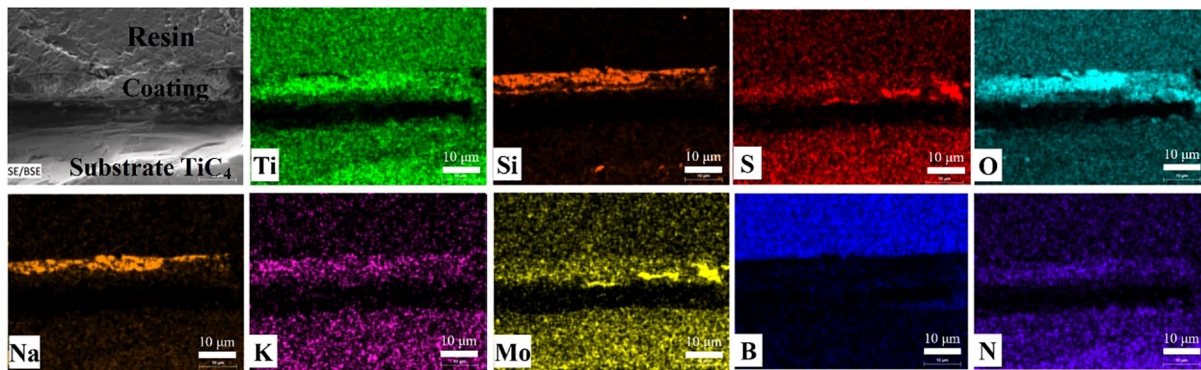


Fig. 6 SEM images and EDS mapping of cross section of worn regions of h-BN-MoS₂-based coating after friction test at 1,000 °C.

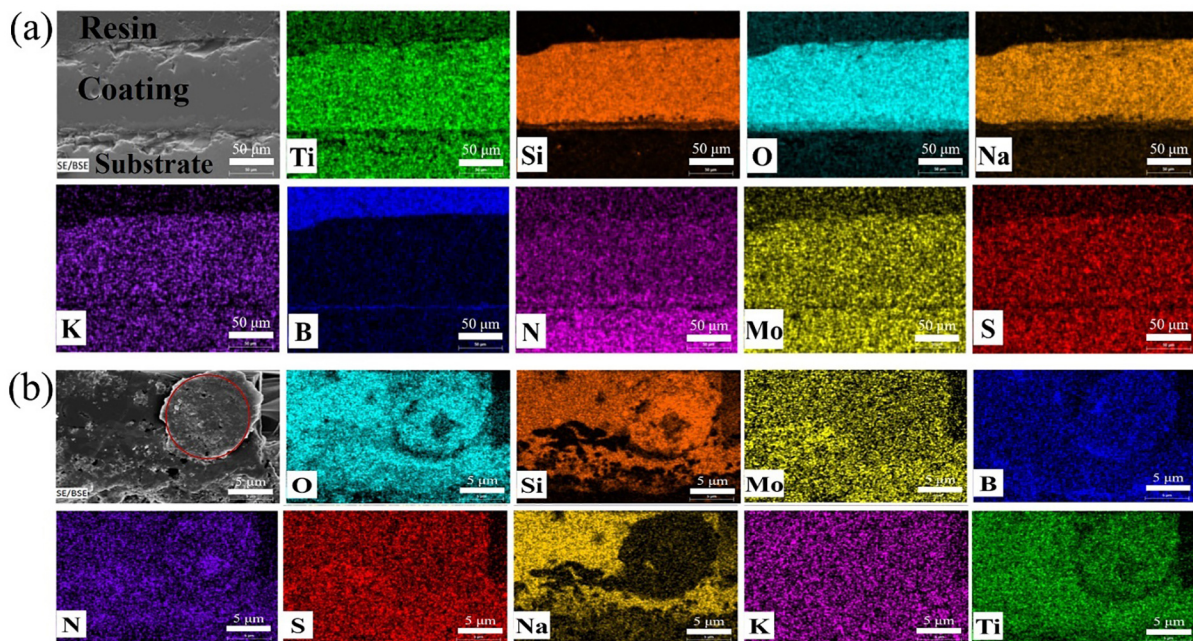


Fig. 7 (a) SEM images and EDS mapping of cross section of non-wear regions of the h-BN-MoS₂-based coating after the friction test at 1,000 °C, and (b) enriched area of h-BN denoted by red circle.

with other components in the coating, which was verified via an increase in the signal intensity of B and N via EDS mapping (Fig. 7(b)).

Overall, the above analysis of the surface and cross section revealed the consistency in the morphology and constituents between the cross section and surface of the wear and non-wear regions. The constituents of the coating were distributed evenly in the bulk and on the surface, and the coating remained intact even at high temperatures if there was no friction shear force. However, the elemental contents and distribution of the coatings under shear force significantly varied. The element Na tended to be enriched on the worn surface, while other elements were preferably distributed across the region with accumulation at the boundary between the coating and substrate. The solid lubricant h-BN was consumed during the friction test via chemical reactions with oxygen, leading to challenges in distinguishing it from other components based on its original morphology and particle size. In addition, the light mass of B and peak overlap between N and Ti, and the adsorbed N further aggravated the difficulty in detecting B and N in the wear regions, and will be discussed in XPS, TOF-SIMS, and TEM sections.

2.4 Chemical analysis

Although EDS mapping demonstrated the existence of elements and their corresponding distributions, the detailed components are still unknown. Therefore, Raman spectroscopy was employed to probe the constituents of the wear regions of different coatings, as well as the reference binder, after the open-air friction test at 1,000 °C (Fig. 8). Detailed information on Raman shifts and corresponding vibrations of the compounds can be found in Table S4 in the ESM. The Raman spectrum of the reference binder was complicated, as indicated by fine peaks and broad humps in Fig. 8(a). The peaks located at 453 and 613 cm⁻¹ were attributed to the active vibration modes of E_g and A_{2g} of rutile TiO₂, and those at 137, 196, 394, and 525 cm⁻¹ were derived from the E_g, E_g, B_{1g}, and B_{1g} modes of anatase TiO₂ [47]. According to Refs. [48, 49], the remaining Raman peaks are composed of three bands associated with Si-related structures: O-Si-O bending vibrations, Si-O symmetric stretching vibrations, and the stretching vibrations of the SiO₄ tetrahedron at 50–550, 550–800, and 800–1,150 cm⁻¹, respectively. Compared with the Raman spectrum, all the Raman peaks of the wear region in the h-BN-based coating (Fig. 8(b)) can be well indexed to those of the reference binder without observable peaks from h-BN and its

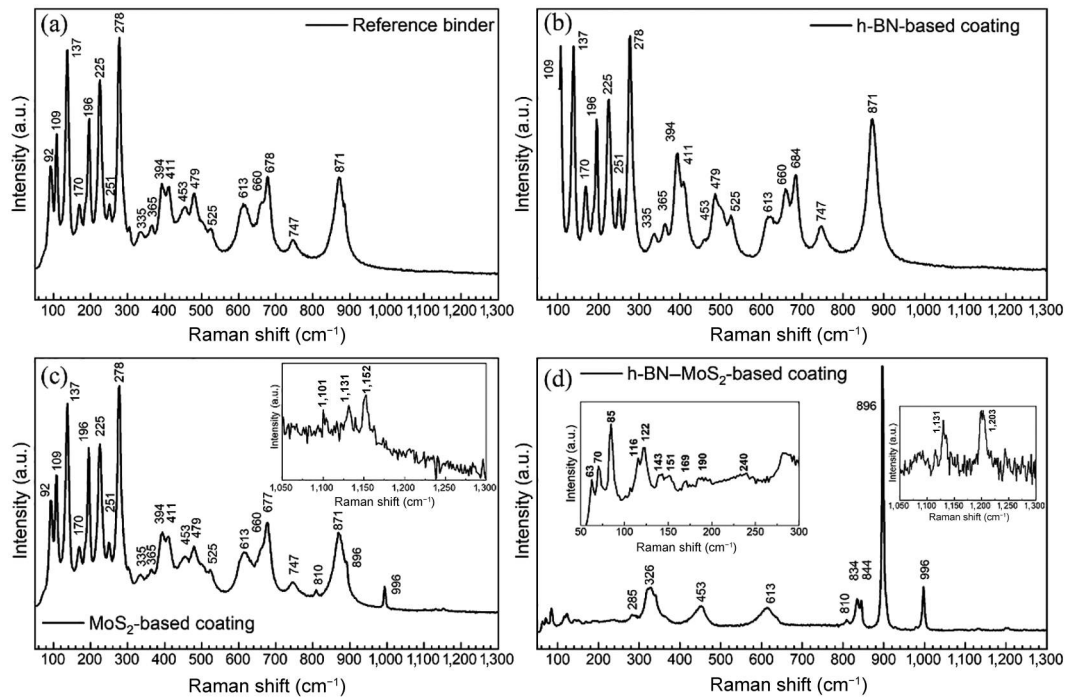


Fig. 8 Raman spectra of the wear regions of (a) reference binder, (b) h-BN-based coating, (c) MoS₂-based coating, and (d) h-BN-MoS₂-based coating after the friction test.

derivatives [48, 50], indicating tiny B- and N-related compounds in the studied region after the friction test. Similarly, most Raman peaks of the wear region in the MoS₂-based coating matched those of the reference (Fig. 8(c)), but with a few small extra peaks located at 996 cm⁻¹ attributed to the symmetric stretching vibration of SO₄²⁻ [51]; at 1,101, 1,131, and 1,152 cm⁻¹ corresponding to the triplet ν_3 asymmetric stretching vibration of SO₄²⁻ [52]; at 896 cm⁻¹ ascribed to the symmetric stretching vibration of MoO₄²⁻ [53]; at 810 cm⁻¹ from the stretching vibration of MoO₄²⁻ [53], highly indicating the presence of SO₄²⁻ and MoO₄²⁻ due to the oxidation of MoS₂ during the high-friction test. In striking contrast; however, the Raman spectrum (Fig. 8(d)) of the wear region in the h-BN-MoS₂-based composite coating was distinct from that of the reference binder, h-BN-, and MoS₂-based coatings and displayed an intense peak at 996 cm⁻¹ from the symmetric stretching vibration of SO₄²⁻ [51], peaks at 1,131 and 1,203 cm⁻¹ from the triplet ν_3 asymmetric stretching vibration of SO₄²⁻ [52], a broad peak at 326 cm⁻¹ from the stretching vibration of MoO₄²⁻ [53], peaks at 810, 834, and 844 cm⁻¹ from the stretching vibration of MoO₄²⁻ [53], and an intense peak at 896 cm⁻¹ from the symmetric stretch vibration of MoO₄²⁻ [53], broad peaks at 143, 453, and 613 cm⁻¹ from the vibration modes of B_{1g}, E_g, and A_{2g} of rutile TiO₂, reflecting that the shallow surface of the coating was mainly composed of sulfate and molybdenite formed during the high-temperature friction test. Notably, the absence of observable peaks from h-BN and its derivatives indicated that their amount was tiny and below the threshold of the Raman technique after the friction test. Overall, the wear region of the h-BN-MoS₂-based coating contained different constituents after the high-temperature friction test from the initial ones, which is consistent with the variation in the surface morphology and EDS results.

As a complement to the Raman study of the wear regions, the Raman spectra of non-wear regions of different coatings and the reference binder were also collected and studied (Fig. S17 in the ESM). The Raman spectrum of the reference binder (Fig. S17(a) in the ESM) demonstrated three weak broad peaks centered at

538 cm⁻¹ due to the O-Si-O bending vibration and at 905 and 1,095 cm⁻¹ corresponding to the stretching vibration of the SiO₄ tetrahedron [48], indicating the presence of an amorphous metasilicate after the friction process, which was congruent with the fact that the reagent metasilicate was the only added component. The Raman peak at 1,367 cm⁻¹ in the spectrum of the h-BN-based coating (Fig. S17(b) in the ESM) was attributed to the characteristic E_g vibration of h-BN [50], reflecting the existence of h-BN in the non-wear regions even at high temperatures. The Raman spectrum of the MoS₂-based coating (Fig. S17(c) in the ESM) showed two prominent peaks at 385 cm⁻¹ (E_{2g}) and 410 cm⁻¹ (A_{1g}), corresponding to in-plane Mo-S vibrations and out-of-plane S-S vibrations [54], respectively, confirming the presence of layered MoS₂ in non-wear regions of the MoS₂-based coating after the friction test. MoS₂ also experienced oxidation reactions, which were reflected by the emergence of broad peaks at 902, 989, and 1,098 cm⁻¹ attributed to the symmetric stretching vibrations of MoO₄²⁻ [53], the symmetric stretching vibrations of SO₄²⁻ [51], and the triplet ν_3 asymmetric stretching vibrations of SO₄²⁻ [52], respectively. In addition, the weak peaks at 110 and 227 cm⁻¹ originating from O-Si-O bending vibrations reflected the presence of the binder silicate [48]. For the h-BN-MoS₂-based coating (Figs. S17(d) and S17(f) in the ESM), a few spots were used to collect Raman spectra to obtain a complete picture. Figure S13(d) in the ESM shows four peaks located at 304, 330, 810, and 834 cm⁻¹ derived from the stretching vibration of MoO₄²⁻ [53, 55]; intense peaks at 892, 898, and 940 cm⁻¹ ascribed to the symmetric stretching vibration of MoO₄²⁻ [53, 55]; a peak at 996 cm⁻¹ from the symmetric stretching vibration of SO₄²⁻ [51]; and peaks located at 1,101, 1,131, and 1,203 cm⁻¹ assigned to the triplet ν_3 asymmetric stretching vibration of SO₄²⁻ [52], confirming the existence of MoO₄²⁻ and SO₄²⁻ from the oxidation of MoS₂ during the friction test. The binder silicate was also deduced based on peaks at 84, 120, and 231 cm⁻¹ from O-Si-O bending vibrations. In addition, the presence of rutile TiO₂ was also indicated by peaks at 457 and 628 cm⁻¹ ascribed to the active vibration modes of E_g and A_{1g} of rutile TiO₂ [47, 56], which may

be due to the nonuniform character of the coating. Figure S12(e) in the ESM reveals the presence of layered MoS₂ in non-wear regions in MoS₂-based coatings after heating on the basis of two prominent peaks at 383 cm⁻¹ (E_{2g}) from in-plane Mo–S vibrations and 409 cm⁻¹ (A_{1g}) derived from out-of-plane S–S vibrations [54]. In addition, the broad peak at 928 cm⁻¹ belongs to the symmetric stretching mode of MoO₄²⁻ [55], confirming the presence of MoO₄²⁻. Figure S12(f) in the ESM shows the presence of the layered h-BN based on the peak at 1,367 cm⁻¹ from the characteristic E_g vibration of h-BN [50]. Overall, the Raman spectra clearly revealed the partial oxidation of MoS₂ in the high-temperature system and the remaining MoS₂ and h-BN in the h-BN–MoS₂-based composite coating system.

It is clear from the Raman spectra that h-BN was not detected in the wear regions of either the h-BN-based or h-BN–MoS₂-based coatings but was detected in the non-wear regions, which agreed well with the observed variation in the surface morphology and elemental distribution. MoS₂ can be oxidized to SO₄²⁻ and MoO₄²⁻ at high temperatures when MoS₂ located in non-wear regions is partially exposed to an air atmosphere, and MoS₂ can be fully oxidized to SO₄²⁻ and SO₄²⁻ under a high-temperature friction shear force. On the basis of the excellent lubrication behavior of the h-BN–MoS₂-based composite coating, the generated MoO₄²⁻ and SO₄²⁻ might be involved in improving the lubrication properties. The detailed role of h-BN in enhancing lubrication behavior was discussed later in the mechanism analysis section.

Given that Raman spectroscopy probes bulk information at a penetration depth of ~1 μm, the XPS technique, which is complementary to the Raman technique, was then employed to study the constituents on the top surface of the wear regions of the coating (Fig. 9 and Fig. S18 in the ESM). Notably, the wear regions were etched for 10 nm prior to data collection to remove surface contaminants such as the absorbed species, and the XPS spectra were then fitted to deduce the oxidation states of different elements. The B 1s spectrum of the wear region in the

h-BN–MoS₂-based composite coating was deconvoluted into one central peak at 192.8 eV and a smaller peak at 190.8 eV (Fig. 9(a)), corresponding to B–O and B–N bonds [57], respectively, and four fitted peaks located at 393.8, 396.5, 398.0, and 398.3 eV in the corresponding N 1s spectrum (Fig. 9(b)) can be attributed to Mo⁴⁺ 3p_{3/2}, N–B bonds, N–O bonds and Mo⁶⁺ 3p_{3/2}, respectively [58–60], indicating the oxidation of h-BN and Mo⁴⁺ during the friction test and the remaining h-BN and Mo⁴⁺ after the test. In comparison, the B 1s spectrum of the wear region in the h-BN-based coating demonstrated a predominant peak centered at 192.5 eV and a tiny peak at 190.8 eV (Fig. S18(a) in the ESM) derived from B–O and B–N bonds [57], respectively, and, similarly, the corresponding N 1s spectrum showed a pronounced peak at 398.0 eV (Fig. S18(b) in the ESM) that was attributed to N–O bonds and a tiny peak at 396.4 eV (Fig. S18(b) in the ESM) that was assigned to B–N bonds, reflecting major oxidation of h-BN during the friction test and negligible h-BN remaining after the test. The Mo 3d XPS spectrum of the wear region in the h-BN–MoS₂-based composite coating was composed of six deconvoluted peaks at 235.1 eV (Mo⁶⁺ 3d_{3/2}), 231.9 eV (Mo⁶⁺ 3d_{5/2}), 233.3 eV (Mo⁴⁺ 3d_{3/2}), 230.1 eV (Mo⁴⁺ 3d_{5/2}), 232.5 (S⁶⁺ 2s), and 228.1 eV (S²⁻ 2s) (Fig. 9(c)) [61, 62], and the fitted peaks of the S 2p XPS spectrum (Fig. 9(d)) located at 169.5, 168.5, 162, and 160.8 eV were ascribed to S⁶⁺ 2p_{1/2}, S⁶⁺ 2p_{3/2}, S²⁻ 2p_{1/2}, and S²⁻ 2p_{3/2} [61, 63], respectively, reflecting the presence of Mo⁶⁺ and S⁶⁺ due to oxidation of MoS₂ during the friction test, which was consistent with the observed Mo⁶⁺O₄²⁻ and S⁶⁺O₄²⁻ from the Raman spectra after the friction test. The XPS spectra (Fig. S19 in the ESM) of Si and O collected from the wear region of the h-BN–MoS₂-based composite coating demonstrated the presence of SiO₃²⁻ [64], indicating that SiO₃²⁻ remained in its original state without being involved in chemical reactions during the friction test. In comparison, the XPS spectra of the h-BN–MoS₂-based composite coating prior to the friction test were also collected (Fig. S20 in the ESM), indicating that the components remained in their pristine

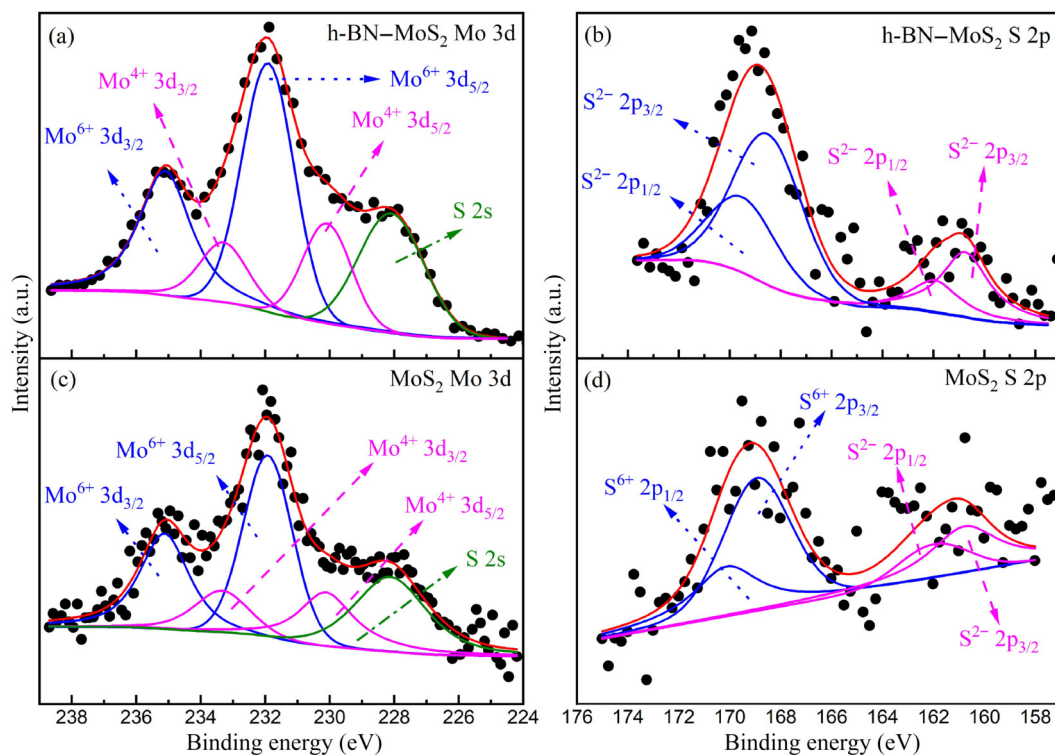


Fig. 9 XPS spectra of (a) B 1s, (b) N 1s, (c) Mo 3d, and (d) S 2p of the wear regions in the h-BN–MoS₂-based coating after the high-temperature friction test.

state [57, 64] and further indicating that the chemical reactions in the h-BN-MoS₂-based composite coating occurred during the high-temperature friction test. In addition, the deconvolution of the Mo 3d and S 2p XPS spectra of the MoS₂-based coating (Figs. S18(c) and S18(d) in the ESM) revealed the same number of fitted peaks for both Mo and S, with almost identical peak positions as those in the h-BN-MoS₂-based composite coating, strongly indicating that the MoS₂-based coating might undergo reactions similar to those of the h-BN-MoS₂-based composite coating. Overall, the XPS spectra of the h-BN-MoS₂-based composite coatings revealed that B, N, Mo, and S were oxidized to boron oxides, nitrogen oxide compounds, MoO₄²⁻, and SO₄²⁻ on the surface of the wear regions, respectively, which is consistent with that reflected by Raman spectra and the presence of remaining h-BN and MoS₂ in the coating.

Given that TOF-SIMS with a probing depth of 1–2 nm is very surface sensitive and powerful for revealing the surface composition and elemental distribution spatially [65], it was herein employed to study the outermost surface of the wear track of the h-BN-MoS₂-based composite coating to complement XPS and Raman techniques, as shown by the gathered mass spectra of positive and negative ion fragments (Figs. S21 and S22 in the ESM) and 2D surface mapping (Fig. 10) under static detection mode and depth profiles (Fig. 11) in dynamic mode. In comparison, the corresponding information of the h-BN-based coating was also collected (Figs. S23–S25 in the ESM). Figures S21 and S22 in the ESM show the secondary ion mass spectra of positive and negative ion fragments, respectively, collected from the wear region of the h-BN-MoS₂-based composite coating after the friction test at 1,000 °C in an open-air system, as well as the corresponding assignment to each peak. The mass spectra clearly revealed the presence of B⁺, B⁺, BO⁺, BO₂⁺, N⁺, N⁺, NO⁺, NO₂⁺, S⁺, S⁺, SO⁺, SO₂⁺, S₂O⁺, S₂O₂⁺, Mo⁺, MoO⁺, MoO₃⁺, MoO₄⁺, Mo⁻, MoO⁻, MoO₂⁻, MoO₃⁻, and MoO₄⁻ on the surface, revealing the presence of B, N, S, and Mo, yet with various oxidation states, as well as O in the tribofilm and further indicating the complicated chemical compositions of the tribofilm on the surface. In addition, the presence of elements from the metasilicate and substrate was

also expected. Figure 10 shows TOF-SIMS 2D-mapping images of vital positive and negative ion fragments in the wear region of the h-BN-MoS₂-based composite coating after the friction test at 1,000 °C in an open-air system. 2D-mapping images revealed the distribution of ion fragments, such as B⁺, BO⁺, BO₂⁺, N⁺, NO⁺, NO₂⁺, S⁺, S⁺, SO⁺, SO₂⁺, S₂O⁺, Mo⁺, MoO⁺, MoO₂⁺, and MoO₃⁺ on the surface. Despite the discrepancies in the concentrations of the ion fragments derived from the color brightness, the ion fragments exhibited roughly uniform distributions across the scanning area without noticeable aggregation, suggesting complete and homogeneous coverage of the tribofilm on the surface of the wear regions. Figure 11 shows the depth profiles of key positive and negative ion fragments gathered from the wear region of the h-BN-MoS₂-based composite coating after the friction test at 1,000 °C in an open-air system. Notably, the sputter depth of negative ion fragments under the same sputtering time was much smaller than that of positive ion fragments because of the different sputter rates. The intensity of B⁺ initially decreased and then increased gradually and reached an apex at ~800 nm inside the surface before decreasing with increasing sputter depth, indicating that the concentration of B⁺ increased from the surface to the bulk. Although the intensity of N⁺ was low, it remained almost constant. From the top surface to the subsurface, Mo⁺ and S⁺ gradually decrease in intensity, yet with a much higher intensity of Mo⁺ probably due to their facile ejection. Even though B⁺, N⁺, Mo⁺, and S⁺ had different distributions with increasing sputter depth, they were still present up to 2 μm into the coating. The negative ion fragments, BO⁻, BO₂⁻, NO⁻, NO₂⁻, S⁻, SO⁻, SO₂⁻, and MoO⁻, exhibited various intensities with different variations associated with the sputter depth. The intensities of BO⁻, BO₂⁻, NO⁻, S⁻, and MoO⁻ initially increased to 18 nm. The intensities of BO⁻, BO₂⁻, and MoO⁻ remained nearly constant before the intensity gradually increased above a sputter depth of 81 nm, whereas the intensities of NO⁻ and S⁻ remained almost unchanged up to 280 nm inside the coating film. The intensities of the remaining secondary ion fragments, NO₂⁻, SO⁻, and SO₂⁻, remained almost constant. The distribution of ion fragments revealed that the dominant species on the surface were B-associated compounds, indicating that

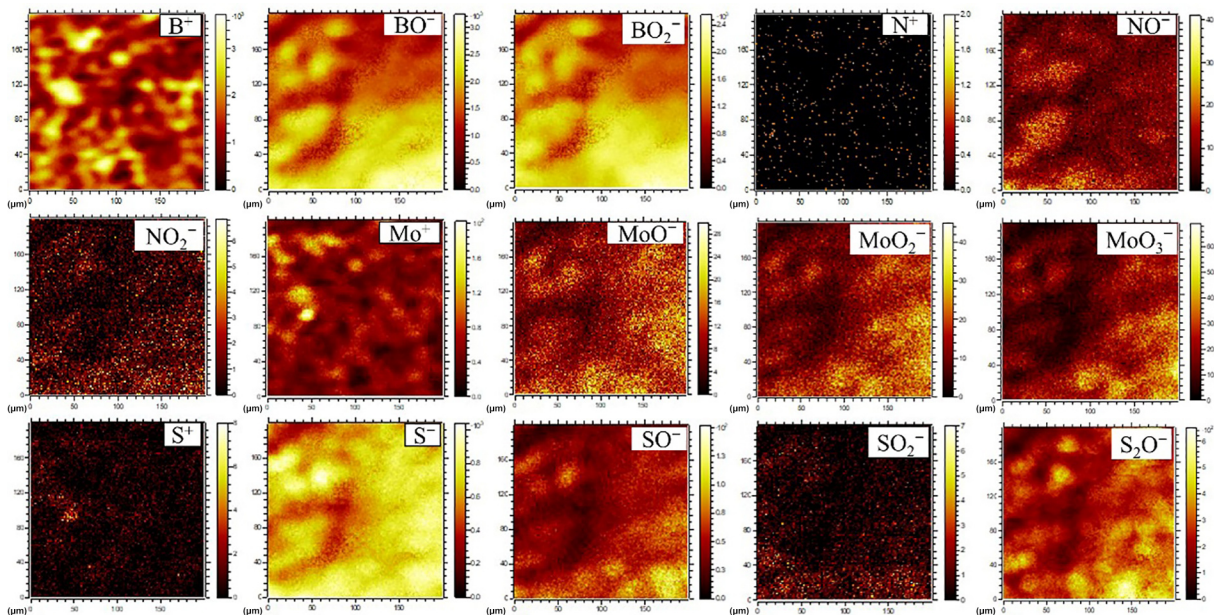


Fig. 10 TOF-SIMS 2D mapping of the vital positive and negative ion fragments detected from the wear region of the h-BN-MoS₂-based composite coating after the friction test at 1,000 °C in an open-air system (scanning area: 200 μm × 200 μm). Note that the chemical distribution related to the binder metasilicate and Ti from the substrate is not included. The color brightness reflects the concentration of the ion fragment. A brighter color represents a higher concentration, whereas a darker color reflects a lower concentration.

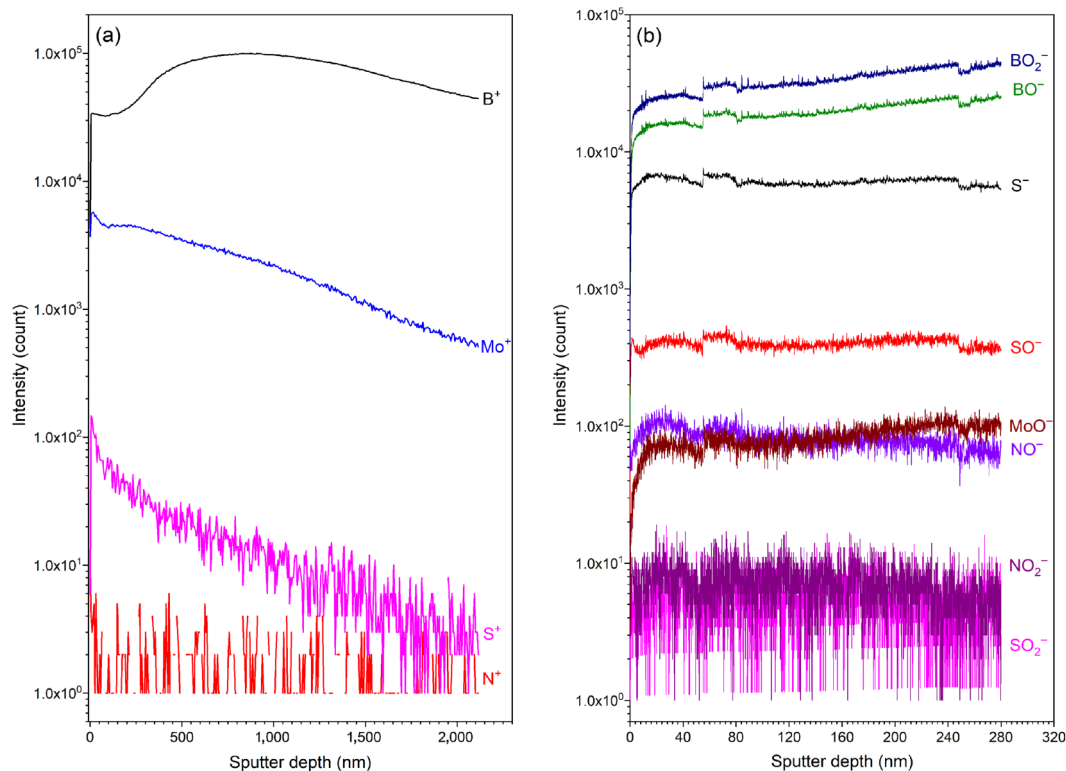


Fig. 11 TOF-SIMS depth profiles showing the evolution of the primary (a) positive and (b) negative ion fragments with sputter depth in the wear regions of the h-BN-MoS₂-based composite coating after the friction test at 1,000 °C in the open-air system. Note that the sudden increase at 55.5 nm and the decrease at 246.8 nm in (b) are due to an instrumental issue and do not affect the conclusion.

h-BN tended to migrate to the surface and preferably took part in oxidation reactions to consume oxygen, and was leaving little for lubrication involvement. In addition, the distribution behaviors of Mo⁺, MoO⁻, S⁺, S⁻, SO⁻, and SO₂⁻ illustrated that MoS₂ also diffused to the surface but with less oxidation than h-BN did, indicating its presence and dominant participation in the lubrication performance on the surface. In addition, the spatial distribution of ion fragments reflected the formation of a stable and relatively thick tribofilm upon the friction test, further supporting the low and stable COF of the h-BN-MoS₂-based coating during the friction test. To better understand the underlying fundamentals of the exceptional lubrication behavior of the h-BN-MoS₂-based coating, the TOF-SIMS data of the wear region of the h-BN-based coating were compared with those of the h-BN-MoS₂-based coating (Section S1 in the ESM). The TOF-SIMS analysis of the ion fragments revealed that the h-BN in the h-BN-based coating diffused into the friction contact zone during the friction test and then was gradually oxidized and consumed due to the high temperature and contact stress to form compounds without lubrication, whereas the h-BN remained in the bulk of the h-BN-MoS₂-based coating. The comparison revealed the fundamentals underlying the different tribological behaviors between the h-BN-MoS₂-based coating and h-BN-based coating, highlighting the synergistic effect of h-BN and MoS₂ on preserving MoS₂ and consequently improving the tribological performance.

2.5 Microstructural analysis

To understand the relationship between the microstructure and lubrication performance, high-resolution TEM combined with the FIB technique was used for sample preparation to probe the microstructures of different coatings. For the h-BN-based coating, EDS mapping revealed that TiO₂ was the predominant

constituent of the surface after the friction test and was almost exposed to the friction pair via direct contact, and that the element Na accumulated on the surface of the worn region (Fig. S26 in the ESM). TEM images further revealed that the main constituents of the coating were amorphous compounds and anatase TiO₂ nanocrystals, as deduced from the characteristic 0.35 nm lattice spacing of the (101) planes from the lattice fringes (Fig. S27 in the ESM) [66]. For the h-BN-MoS₂-based coating after the friction test, there was a layer of accumulated Mo with a thickness of approximately 1 μm, and many regions of Mo accumulated beneath the coating (Fig. S28 in the ESM). In comparison, the other elements were uniformly distributed in the coating (Fig. S28 in the ESM). However, the microstructure of the Mo-enriched layer was not studied because of the coverage of Pt used to protect the loose Mo-rich layer from delamination during the FIB process (Figs. 12(a) and 12(b)). However, MoS₂ inside the coating displayed no deformation and still retained its original layered structure, with an interlayer spacing of ~0.627 nm close to the characteristic lattice spacing of ~0.62 nm for the (002) planes of bulk MoS₂ (Fig. 12(c)) [67].

In pursuit of better probing the microstructure of the Mo-rich surface layer, a small piece of the surface layer was peeled off from the h-BN-MoS₂-based composite coating and then loaded on the microgrid for high-resolution TEM experiments. EDS mapping via TEM revealed a relatively uniform distribution of elements in the coating (Fig. S29 in the ESM). Notably, some S-rich regions with less Mo existed, indicating that S and Mo did not exist in the form of MoS₂, which was confirmed by the presence of areas rich in either S only or Mo only in the EDS spectra (Fig. S30 in the ESM), which is consistent with the aforementioned analysis. In addition, signals from the elements N and B were also observed (Fig. S29 in the ESM). Given the weak signal of Ti from EDS mapping, the noticeable signals of B and N indicated the presence

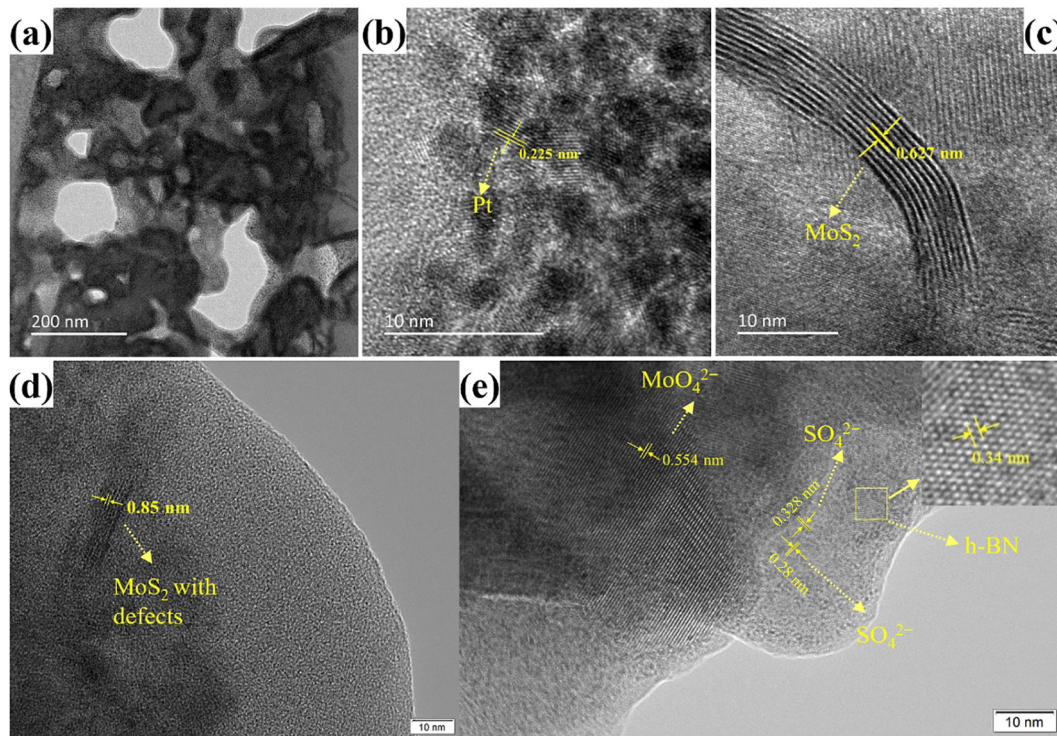


Fig. 12 High-resolution TEM images of the wear region of the h-BN-MoS₂-based coating. (a–c) FIB-prepared cross section and (d, e) peeled-off piece.

of N and B, which is reminiscent of the remaining h-BN and is consistent with the XPS and TOF-SIMS results. High-resolution TEM revealed that the lattice fringes with an interplanar distance of ~ 0.85 nm in the Mo-rich surface region were close to the lattice spacing of the (002) planes in MoS₂ with high-temperature-induced defects during the friction test (Fig. 12(d)) [68]. In addition, a few other lattice fringes were observed in high-resolution TEM images of worn regions with different interplanar distances (Fig. 12(e)). The lattice fringes with an interplanar distance of 0.554 nm corresponded to the lattice spacing of the (110) lattice planes in SO₄²⁻ (PDF#30-1286). The interplanar distances of 0.328 and 0.28 nm were close to those of the (220) and (311) lattice planes in MoO₄²⁻ (PDF#12-0073) [55], respectively, confirming the presence of MoO₄²⁻, which was again consistent with the Raman and XPS results. The combination of an interplanar distance of 0.34 nm (an inset in Fig. 12(e)) and the corresponding SAED from the yellow square region (Fig. S31 in the ESM) indicated the presence of h-BN due to the matched lattice spacing of the (002) planes in h-BN (PDF#34-0421) [69], which was consistent with the Raman, XPS, and TOF-SIMS analyses. Notably, it was difficult to visualize boron oxide (B₂O₃) even with high-resolution TEM because of its amorphous nature after the high-temperature friction test.

Based on the above analyses, the mechanism accounting for the excellent lubrication performance of the h-BN-MoS₂-based coating was proposed as follows. The lubricant MoS₂ on the coating surface underwent oxidation reactions with oxygen to form MoO₄²⁻ and SO₄²⁻ during the rising and holding periods, whereas the h-BN powders grew into large flakes. Upon high-temperature friction testing under applied loading, the formed MoO₄²⁻ and SO₄²⁻, the layered MoS₂ on the surface, and the flaky h-BN on the surface fused to generate a lubrication coating as a tribofilm. In the friction test, MoS₂ and h-BN on the surface were gradually consumed, which was complemented by the diffusion of MoS₂ and h-BN from the bulk of the coating. Moreover, h-BN acted as an anti-oxygen reagent to protect MoS₂ from further

oxidation. The combination of consumption, complement, and protection resulted in a stable tribofilm within the time scale of the friction test, which enabled excellent lubrication performance under an open-air friction test system at 1,000 °C. In addition, the study of the effects of boron oxides as additives on the tribological performance of MoS₂ has already been conducted by Kelenke in 1990 and illustrated that at temperatures higher than the softening point of boron oxides at ~ 253 °C, the easy removal of MoS₂ from the interface with the substrate, due to the dramatic decrease in the viscosity of boron oxides, led to poor lubrication performance [70], further confirming the indispensability of the base lubricant h-BN and that the synergistic effect of h-BN and MoS₂ leads to superior lubrication of the h-BN-MoS₂-based solid lubricant coating.

3 Conclusions

In summary, we prepared an h-BN-MoS₂-based solid lubricant coating in a facile and eco-friendly fashion, which displayed excellent lubrication performance with strong adhesion to the substrate and a very low and stable coefficient of friction (COF) of ~ 0.080 at a high temperature of 1,000 °C in an open-air atmosphere. The scanning electron microscopy (SEM) morphology and energy dispersive X-ray spectroscopy (EDS) mapping of the surface and cross section of the wear and non-wear regions revealed a uniform elemental distribution across the whole coating. The component analyses of the composite coating after the friction test via Raman and X-ray photoelectron spectroscopy (XPS) spectra demonstrated both the existence of the remaining base lubricants (h-BN and MoS₂) and the presence of the corresponding oxidation products, including boron oxides, nitrogen oxides, MoO₄²⁻, and SO₄²⁻. A nearly homogeneous distributions of these species on the surface were confirmed via the complementary time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis. The microstructural analysis of the coating after the friction test further confirmed the presence

of the remaining base lubricants, h-BN, and MoS₂, yet with a layered structure fundamental for excellent lubrication. The formation of a solid coating on the surface from a mixture of MoO₄²⁻, SO₄²⁻, and boron oxides, nitrogen oxides, MoS₂, and h-BN upon high-temperature friction test suggested that the solid coating acted not only as a tribofilm with superior lubrication properties but also as a barrier layer blocking the diffusion of oxygen into the bulk. Moreover, h-BN was also synergistically involved as an antioxidant to protect MoS₂ from being continuously oxidized upon friction. This work largely broadens the temperature range of the critical lubricant MoS₂ in an open-air system and further sheds light on the design of high-temperature solid lubricants by employing a synergistic effect.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. The author Chenhui Zhang is the Editorial Board member of this journal.

Electronic Supplementary Material

Supplementary material ((i) experimental; (ii) Sections S1 and S2; (iii) supplementary figures: Figs. S1–S31; (iv) supplementary tables: Tables S1–S4) is available in the online version of this article at <https://doi.org/10.26599/FRICT.2025.9441067>.

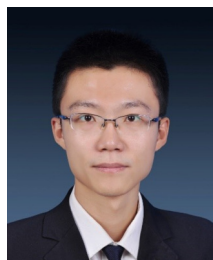
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